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Partial molar volumes of organic solutes in water. XXIII. Cyclic ketones at T = (298 to 573) K and pressures up to 30 MPa

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ABSTRACT

Density data for dilute aqueous solutions of four cyclic ketones (cyclopentanone, cyclohexanone, cycloheptanone, and cyclohexane-1,4-dione) are presented together with standard molar volumes (partial molar volumes at infinite dilution) calculated from the experimental data. The measurements were performed at temperatures from T = 298 K up to T = 573 K. Experimental pressures were close to the saturated vapor pressure of water, and (15 and 30) MPa. The data were obtained using a high-temperature high-pressure flow vibrating-tube densimeter. Experimental standard molar volumes were correlated as a function of temperature and pressure using an empirical polynomial function. Contributions of the molecular structural segments (methylene and carbonyl groups) to the standard molar volume were also evaluated and analyzed.

1. Introduction

This paper is a part of our series of the systematic experimental studies of partial molar volumes of organic solutes at infinite dilution in water (standard molar volumes). In the previous papers experimental results for standard molar volumes of two groups of cyclic aliphatic solutes (cycloalkanols [1,2], cyclic ethers [3,4]) have been published. Recently the data for cyclic ketones (cyclopentanone, cyclohexanone, cycloheptanone, and cyclohexane-1,4-dione) in the temperature range from (278 to 373) K under either atmospheric pressure or pressure 0.5 MPa were reported [5]. New data presented here are an extension of the results obtained in the ambient and close-to-ambient range of state parameters to superambient conditions and enable us to extend the applicability of the group contribution scheme [3,4] proposed previously for the estimation of standard molar volumes of cyclic ethers.

2. Experimental

The organic solutes were those used previously [5], *i.e.*, cyclopentanone (Fluka, stated mass purity greater than 0.99), cyclohexanone (Sigma–Aldrich, stated mass purity 0.998), cycloheptanone (Aldrich, stated mass purity 0.99), and cyclohexane-1,4-dione (Fluka, stated mass purity greater than 0.98) were used without further treatment. Details concerning the experimental technique and methodology can be found in the previous papers [3,4], here a brief summary only is given. The high-pressure high-temperature densimeter [6–8] working in the automated flow regime [8] with a high-pressure pump adjusted to the flow rate of 0.6 $cm^3 \cdot min^{-1}$ was used for the measurements. Repeated calibrations of the densimeter were performed at each experimental temperature and pressure using water and nitrogen whose densities were taken from the literature [9,10]. The thermostated back-pressure regulator [8] was connected to the end of the pressure line. The maximum systematic error of the measured density differences $\Delta\rho = \rho - \rho_1$ resulting from the densimeter calibration was about 0.2% and the reproducibility of the measurements was within $\pm 3 \cdot 10^{-3}$ $kg \cdot m^{-3}$ in most cases. The temperature of the densimeter cell was measured using a calibrated (ITS 90) platinum resistance thermometer (BURNS Engineering), with a resistance R_0 = 100 Ω at T = 273.15 K, connected to a multimeter in a four-lead configuration. The resolution of the temperature measurements was 0.1 mK. Temperature stability of the cell during one experiment (measurement of one sample) was within 1 mK. The total uncertainty of the temperature measurements was

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